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THE REACTIONS OF FREE RADICALS IN SOLUTION  
A TECHNICAL PROGRESS REPORT  
ONR CONTRACT

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During the period from March 15, 1951 to the present time work under this project has been conducted with three general objectives. The first is the investigation of the reactions of the primary products of thermal decomposition reactions in order to help establish generalizations concerning relative reactivity and mechanism in free radical reactions. The second, while novel and highly interesting in its own right, is actually a necessary step in the interpretation of our results in terms of our first objective. This is the study of effects which are unique to thermal decomposition in that they are due to the occurrence of diffusion controlled reactions of two primary decomposition products with each other. The last objective has been the study of the reactions of triphenylmethyl with various organic compounds in the hope that information could be obtained which would shed light on the behavior of more reactive radicals.

Progress toward the first two objectives may be considered normal and gratifying. The third line of endeavor has been disappointing in that a great deal of time has been expended in a reinvestigation of the behavior of triphenylmethyl in the presence of nitrobenzene. Results which were reported earlier

by Dr. Raave have been impossible to repeat with the result that implications of considerable significance which had previously been drawn must now be considered to be unfounded.

It is hoped that the work can be continued and a proposal has been submitted to the National Science Foundation with the hope that that agency will be able to support a continuation of these studies. The generous support of the Office of Naval Research has been much appreciated. Without such support much of our work would have been impossible. Three post-doctoral fellows have been employed on the project. They are Dr. Louis Soffer, now senior chemist at Aberdeen Proving Ground, Dr. Raave whose present connection is unknown, and Dr. Jyotirindra N. Sen who is on leave of absence from the Calcutta Institute for the Advancement of Science. One graduate student, Dr. George B. Lucas, has completed a doctoral dissertation from his studies and has been granted his Ph.D. degree. He is at present a senior chemist with the Redstone Arsenal Research Division of the Rohm and Haas Company. A second student, Mr. John Tanaka, has made a substantial start on his doctoral research under the contract. In addition, Dr. Charles E. Boozer who has been employed under another grant has contributed to the work by supplying data on the rate of decomposition of azo-bis-isobutyronitrile in various solvents and by helpful consultation.

Part of the work is reported and discussed in a copy of a long abstract which has been accepted by the Physical and

Inorganic Division of the American Chemical Society for presentation at the Kansas City Meeting in March. This paper is, in essence, a first draft of a manuscript which we hope to submit for publication in the near future. Manuscripts are also in preparation which will report the studies of the polymerization of methacrylonitrile and of the decomposition of azonitriles in the presence of chloranil. Publication on the latter subject is to be delayed, however, as Dr. Lucas is currently checking related results recently reported by other workers which are surprising in the light of our observations. Other work must be further elaborated before it is suitable for publication.

#### Experimental

Toluene (Baker and Adamson, Reagent Grade) was distilled through a six-foot column packed with glass helices. The fraction boiling at 109-110° (uncorr.) was used in subsequent work.

Cumene (Eastman Kodak White Label) was distilled using a Vigreux still head. The liquid boiling at 151.5-152° (uncorr.) was stored over calcium metal chips and used throughout.

Tetralin (Eastman Kodak White Label) was distilled at 91°/18 mm. through a six-foot helix packed column.

Chlorobenzene (Paragon Division, Matheson Chemical Co.) was used without further purification.

Chloranil (Eastman Kodak Yellow Label) was recrystallized from glacial acetic acid and dried over sodium hydroxide in a vacuum desiccator.

Azo-bis-diethylacetonitrile was prepared by the method of Dox(1). The yield was 60 per cent, m.p. after two

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(1). A. Dox, J. Am. Chem. Soc., 47, 1473 (1925).

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recrystallizations from ethanol, 74-5°.

Azo-bis-isobutyronitrile was prepared by the method of Dox (1) in 70 per cent yield. After two recrystallizations the product melted at 101-2°.

ω, ω'-Azo-bis-toluene - was prepared by the method of Bickel and Waters (2). The product was never obtained in a high state

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(2) Bickel and W. A. Waters, Rec. Trav. Chim, 69, 312 (1950).

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of purity but seemed to be contaminated by a high melting by-product (~127-30°) which was believed to be benzalbenzylhydrazone. However, after a number of recrystallizations from 95 per cent ethanol in a dry ice-acetone bath, a product melting at 31-3° [lit. (2)] was obtained.

Di-t-butyl peroxide, donated by the Shell Development Corporation, Emeryville, California, was distilled through a 44 plate glass center-rod column (45°/20 mm.) before use.

Cumene hydroperoxide (79 per cent in cumene) donated by the Hercules Powder Company was purified by first precipitating the sodium salt by shaking with 50 per cent aqueous sodium hydroxide and neutralizing exactly with 2N sulfuric acid (3). After

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(3) Hock and Lang, Ber., 77, 257 (1944).

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washing with potassium carbonate solution to insure complete removal of acid, the material was distilled at  $41^{\circ}/0.01$  mm. The product gave 98 per cent of the theoretical iodometric titer.

Cumyl alcohol was prepared by the method of Kharasch et. al. (4)

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(4) M. S. Kharasch, Fono and Nudenberg, J. Org. Chem., 16, 113, (1951).

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from cumene hydroperoxide. The product, after distillation through the center-rod column and three recrystallizations from petroleum ether, melted at  $36-36.5^{\circ}$ .

Di- $\alpha$ -cumyl peroxide was prepared by thermal decomposition of cumene hydroperoxide in  $\alpha$ -cumyl alcohol at  $95^{\circ}$  (5). Although

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(5) M. S. Kharasch, Fono and Nudenberg, ibid. 15, 753 (1950).

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it is reported that near quantitative yields can be obtained we were able to obtain only 5-10 per cent. After recrystallization from ethanol in a dry-ice-acetone bath the product melted at  $39.0-39.5^{\circ}$ .

t-Butyl hydroperoxide was prepared by the method of Milas and Surgenor (6). It was separated from the dialkyl peroxide

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(6) Milas and Surgenor, J. Am. Chem. Soc., 68, 207 (1946).

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by precipitation of the sodium salt and neutralization with 2N sulfuric acid.

Decomposition of Azo-bis-diethylacetonitrile in Toluene.

Three and three tenths g. (0.015 mole) azo-nitrile was dissolved in 50 ml. toluene and the solution was refluxed for 15 hours. The toluene was then stripped under reduced pressure at head

temperatures below 50°. After 3-4 hours at room temperature the residue deposited crystals of tetraethylsuccinonitrile. The distillation of toluene was then resumed and after the removal of a small amount a second crop of dinitrile was obtained. The total yield was 2.09 g. (73 per cent) which melted at 47-48° after recrystallization from ethanol-water. Neither the distillate nor recrystallization residues appeared to contain sym-diphenylethane.

Decomposition of Azo-bis-diethylacetonitrile in Toluene containing Chloranil. Two and two tenths g. (0.010 moles) of azo-bis-diethylacetonitrile and 2.48 g. (0.010 g.) chloranil were dissolved in 100 ml. toluene and heated at reflux for 15 hours. The solution was then cooled and extracted with five per cent aqueous sodium hydroxide until the extract was colorless. The extract was deep red in color due to the formation of chloranilic acid. Upon acidification with five per cent hydrochloric acid a dirty brown solid was precipitated. After repeated recrystallization from glacial acetic acid this product gave white crystals of tetrachlorohydroquinone monobenzyl ether. The yield was 0.53 g. (16 per cent). Anal. calc. for  $C_{13}H_8O_2Cl_4$ : C, 46.3; H, 2.47; Cl, 42.1; found; C, 46.6; H, 2.48; Cl, 41.6 (7).

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(7) All analyses by Drs. Weiler and Straus, Microanalytical Laboratory, Oxford, England.

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The organic layer from the extraction was steam distilled and the distillate which contained all of the toluene was



extracted with ether and the extract was dried over anhydrous sodium sulfate. After drying, the toluene-ether mixture was distilled under reduced pressure as in the previous experiment. The residue, worked up as in the control, gave 0.6 g. (31 per cent) tetraethylsuccinonitrile.

The residue from the steam distillation was recrystallized from a large volume of ethanol and gave 1.55 g. (45 per cent based on azonitrile) tetrachlorohydroquinone di-(3-cyano-3-pentyl) ether, m.p. 166-7°. Anal. calc. for  $C_{18}H_{20}O_2N_2Cl_4$ ; C, 49.3; H, 4.56; Cl, 32.4; N, 6.39; found C, 50.1; H, 4.42; Cl, 31.7; N, 6.32.

Decomposition of Azo-bis-diethylacetoneitrile in Chlorobenzene Containing Chloranil. The reaction was carried out and products were isolated by a procedure essentially identical with that described above for the experiment in toluene. The phenolic product obtained was not identical with that obtained in toluene solution and, on the basis of elementary analysis, was assigned the structure tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether, m.p. 165°. Anal. calc. for  $C_{12}H_{11}O_2NCl_4$ ; N, 4.08; Cl, 41.4; found; N, 4.17; Cl, 40.7.

Yields and material balance are included in Table I.

Decomposition of Azo-bis-isobutyronitrile in toluene containing Chloranil. The decomposition was carried as above. The solution after heating was extracted with 10 per cent aqueous sodium hydroxide. On acidification the extract gave an amorphous precipitate. The solid was separated into two

constituents by fractional crystallization from glacial acetic acid. The less soluble constituent was the monobenzyl ether of tetrachlorohydroquinone identical with the material produced in the similar experiment with Azo-bis-diethylacetonitrile. Samples from the two runs gave no mixed melting point depression and had identical infrared spectra. The mother liquors from the separation of the benzyl ether gave a material which was amorphous but had an infrared spectrum identical with that of an authentic sample. The spectrum showed no significant absorption at 13.25 microns showing the absence of the monobenzyl ether.

The steam distillate from the reaction mixture was examined for bibenzyl in the following manner. The last fraction from the recrystallization of tetramethylsuccinonitrile was dried and the infrared spectrum was determined in a Nujol mull. The spectrum was identical to that of pure dinitrile and showed no absorption at 13.25 microns (characteristic of all benzyl compounds studied including bibenzyl). The steam distillation residue gave tetrachlorohydroquinone di-(2-cyano-2-propyl) ether, however, no m.p.  $166^{\circ}$ . The crude residue gave a spectrum which had no absorption at 13.25 microns.

Decomposition of Azo-bis-isobutyronitrile in Chlorobenzene containing Chloranil was carried out and the products were worked up as described for other experiments. Yields are summarized in Table I.

Attempted Syntheses of Tetrachlorohydroquinone Mono Benzyl Ether. Several attempts were made to prepare this compound by

the alkylation of the hydroquinone with benzyl chloride. With aqueous or alcoholic sodium hydroxide or with potassium carbonate and dry-acetone only unreacted hydroquinone and the diether could be isolated. With sodium hydride in dry ether the starting materials were recovered unchanged.



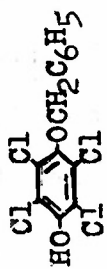

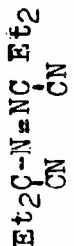
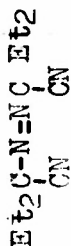



Preparation of tetrachlorohydroquinone dibenzyl ether.

Eight g. (0.03 mole) tetrachlorohydroquinone was added to 2.6 g. (0.065 moles) sodium hydroxide in 100 ml. water. The solution was heated to reflux and 9.0 g. (0.07 mole) benzyl chloride was added dropwise. After the addition was complete the solution was refluxed for two more hours. On cooling a precipitate formed which was recrystallized from 95 per cent ethanol, m.p. 173.5-173.8°. Anal. calc. for  $C_{20}H_{14}O_2Cl_4$ ; C, 56.0; H, 3.28; Cl, 33.2; found; C, 57.8; H, 3.47; Cl, 31.8.

Structure of Tetrachlorohydroquinone Monobenzylether. The potentiometric titration of the substance in water solution indicated an equivalence point at pH 8.4. The neutral equivalent found was 332 as compared with the calculated value of 337. Since the compound could not be made easily by alkylation the monoether was converted to the diether. A 0.5 g. sample of the product from the decomposition of azo-bis-diethylacetonitrile in toluene containing chloranil was dissolved in the minimum volume of five per cent aqueous sodium hydroxide and heated to reflux. The 0.2 ml. benzyl chloride was added dropwise and the solution was refluxed for four hours. A solid separated during the heating period and after cooling it was extracted

TABLE I

Decomposition of Azonitriles in the Presence of Chloranil

Azonitrile	Moles Azonitrile X10 <sup>2</sup>	Moles Chloranil X10 <sup>2</sup>	Solvent (50 ml.)	Yields (moles x 10 <sup>2</sup> )			
							R-R
	1.5	None	toluene				1.09
	0.5	1.3	toluene	0.45		0.08	0.31
	1.3	1.3	Chloro- benzene	0.67	0.66		0.47
	1.0	None	toluene				0.86
	0.94	1.0	toluene	0.27	0.036	0.032	0.36
	1.1	0.53	Chloro- benzene	0.29	0.037		0.46

with ether. The ether was evaporated and the solid residue was recrystallized from 95 per cent ethanol, m.p. 173-5° no depression on admixture with authentic material. The infrared spectrum was also identical with that of the authentic material.

Alkylation of tetrahydroquinone mono (3-cyano-3-pentyl) ether.

The proof of structure of the monobenzyl ether by conversion to the dibenzyl ether involves the assumption that some other ether would not be cleaved and then dibenzylated under the reaction conditions. Since it is especially important to demonstrate that the substance was not the cyanoalkyl ether a small sample of the latter compound was benzylated under identical conditions. The white product was recrystallized from methanol and melted at 230-50° but depressed the melting point of authentic dibenzyl ether.

Decomposition of *o,o'*-azotoluene in Toluene containing Chloranil. A 2.46 g. (0.014 mole) sample of chloranil and 0.21 g. (0.001 mole) impure azo-bis-toluene were dissolved in 500 ml. toluene and heated to reflux for 48 hours. After cooling, the solution was extracted with 10 per cent sodium hydroxide until the extracts were clear. Acidification of the aqueous extract with dilute sulfuric acid gave 0.29 g. (0.0009 mole) of monobenzyl ether which after recrystallization from glacial acetic acid melted at 139-40°. No products could be isolated from the tarry residue from steam distillation of the oil phase from the extraction.

Determination of Ketones. The determinations were carried out by a variation of the method of Siggia (8). An aliquot of

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- (8) Siggia, "Quantitative Analysis via Functional Groups", John Wiley and Sons, Inc., New York (1949); p. 17.
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the test solution was pipetted into 50 ml. of a hydroxylamine hydrochloride solution (35 g. in 160 ml. distilled water diluted to one liter with 95 per cent ethanol). The liberated hydrochloric acid was titrated potentiometrically with either 0.2 or 0.5 N standard aqueous sodium hydroxide. The precision of the determination, evaluated by synthetic mixtures, was  $\pm 5$  per cent.

For those samples which contained both acetone and acetophenone the total ketone and acetone contents were determined in separate samples. For the latter the sample was pipetted into a special distilling flask equipped with a long right angle side arm containing a condenser in the vertical portion. Ten ml. benzene (Baker and Adamson, thiophene free, reagent grade) was added as a carrier. The acetone and benzene were then distilled over a water bath into 50 ml. hydroxylamine hydrochloride solution. This solution was then titrated as described above.

Determination of Alcohols. Methyl lithium (9) dissolved in

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- (9) H. Gilman, Zoellner and Selby, J. Am. Chem. Soc., 55, 1252 (1933).
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in di-n-butyl ether, was first equilibrated in a flask equipped with a magnetic stirrer and connected to a gas buret, until the volume of gas no longer varied (2-3 hours). After equilibration,

one or two ml. of the sample was injected through a rubber nipple by means of a hypodermic syringe. The solution was stirred and the volume was measured after variation caused by the heat of the reaction had ceased. A blank of 0.87 ml. for each ml. of solution was determined empirically and was subtracted from each determination. The precision was  $\pm 10$  per cent.

Decomposition of Peroxides. The peroxide was weighed in a 50 ml. volumetric flask (approximately 20 millimoles per 50 ml.) and diluted to the mark with cumene. Mixtures of di-tert-butyl peroxide and di- $\alpha$ -cumyl peroxide were prepared by dissolving approximately 20 millimoles di-tert-butyl peroxide and a calculated amount of the cumyl peroxide in 50 ml. The amount was calculated to give approximately equal concentrations of cumyloxy and tert-butoxy radicals at the beginning of the run. The calculations were based upon reported first order rate constants<sup>10,11</sup>. The peroxide sample to be decomposed was

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(10) Raley, Rust and Vaughan, *ibid.*, 70, 88, 95 (1948).

(11) Kharasch, Fono and Nudenberg, *J. Org. Chem.* 16, 105 (1950).

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pipetted from the volumetric flask into a round bottomed, long-necked flask with a constriction in the neck. The flask was chilled in an ice bath and evacuated with a Cenco Hyvac pump. The flask was sealed at the constriction while still evacuated and allowed to come to room temperature. The flask was then immersed in a thermostated oil bath ( $132.5 \pm 0.2^\circ$ ) for a period

calculated to give more than 99 per cent completion<sup>12</sup>. From the

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(12) It was assumed that triphenylmethyl-tert-butyl peroxide decomposed at a rate comparable to that of di-tert-butyl peroxide.

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decomposition residues bi- $\alpha$ - cumyl, m.p. 117-8°, was isolated.

The decomposition of triphenylmethyl tert-butyl peroxide always gave a yellow solution. From the residue, besides bi- $\alpha$ - cumyl, an impure white solid, m.p. 164-6°, was isolated. The infrared spectrum was similar to that of triphenyl carbinol and is believed to contain benzpinacol-diphenyl ether.

The solutions were analyzed for ketones and alcohol as described above. The results are summarized in Table II.



TABLE II

Decomposition of Di-tert-alkyl Peroxides (ROOR') in Cumene at 172°.

Run	R	R'	Moles Peroxide X10 <sup>3</sup>	Moles Ketone X10 <sup>3</sup>	Moles Alcohol X10 <sup>3</sup>	Per Cent Ketone	Per Cent Alcohol
1	t-Bu	t-Bu	20.47	7.25	31.25	17.7	74.5
2	t-Bu	t-Bu	24.00	8.10		16.9	
3	$\phi_3C$	t-Bu	16.80	3.19	30.0	19.0	89.5
4	$\phi C(CH_3)_2$	$\phi C(CH_3)_2$	0.148	0.247		81	
5	t-Bu $\phi C(CH_3)_2$	t-Bu $\phi C(CH_3)_2$	24.91 0.0819	10.30 <sup>b</sup>	43.8	19.8	87.5
6	t-Bu $\phi C(CH_3)_2$	t-Bu $\phi C(CH_3)_2$	28.15 0.0912	9.96 <sup>c</sup>	48.8	17.8	84
7	t-Bu $\phi C(CH_3)_2$	t-Bu $\phi C(CH_3)_2$	24.3 0.099	10.58 <sup>b</sup>		21.8	
8	t-Bu t-Bu	t-Bu $\phi_3C$	22.42 20.05	15.20	59.09	23.4 <sup>a</sup>	69.5
9	t-Bu t-Bu	t-Bu $\phi_3C$	25.59 5.343	11.58	46.52	20.3	75.0

a. Ketone yield calculated on basis of t-butoxy radical.

b. Total ketone.

c. Acetone only.

TABLE III

Apparent Rates of AIBN Decomposition Measured by DPH  
Disappearance in Carbon Tetrachloride

Run	$[\text{DPH}]_0 \times 10^3$ (m./l.)	$[\text{AIBN}]_0 \times 10^2$ (m./l.)	T	$t_c$ (min)	$k_1 \times 10^6 \text{ sec.}^{-1}$
43	0.278	2.640	60	27	3.25
44	.278	3.96	60	18.5	3.17
45	.511	3.961	60	29	3.71
46	.128	1.321	60	22	3.67
51	.128	1.309	60	25	3.32
54	.0639	0.639	60	22	3.49
56	.0639	.346	60	42.6	3.61
57	.0639	.419	60	29.5	3.47
62	.630	4.854	60		10.54 <sup>1</sup>
102	.0773	.492	62.5	31.5	4.16
100	.124	.656	62.5	34	4.6
103	.0773	.492	62.5	43.5	3.09 <sup>2</sup>
81B		5.23	62.5		11.8 <sup>1</sup>

1. Rate of decomposition by nitrogen evolution.
2. Sealed tube.

TABLE IV

Apparent Rates of AIBN Decomposition Measured by  
DPH Disappearance in Chlorobenzene

Run	T	$(DPH)_0 \times 10^3$ (m/l)	$(AIBN)_0 \times 10^2$ (m/l)	$t_c$ (min)	$k_1 \times 10^6$
68	60	0.143	0.649	27	6.82
69	60	0.0717	.325	26	7.08
70	60	0.0717	.195	40.5	7.57
71	60	0.0717	.455	25.25	6.83
72	62.5	0.0717	.195	30	10.2
76	62.5	0.0717	.257	23.5	9.79
71B	62.5		15.20		15.4 <sup>1</sup>
97	62.5	.133	.615	27.5	6.54 <sup>2</sup>
106	74.4	.0665	.0661	29.25	28.67
83B	74.4		15.20		78 <sup>1</sup>

1. Rate of decomposition by nitrogen evolution.

2. Sealed tube.

Triphenylmethyl. The triphenylmethyl was prepared from triphenylcarbinol via triphenylchloromethane. The carbinol was carefully purified, the steam distilled residue being recrystallized several times from ethanol. The triphenylchloromethane was made according to the Organic Synthesis procedure<sup>13</sup>. The

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13. Organic Synthesis, vol. 23, p. 100.

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triphenylmethyl radical was then generated by vigorously stirring the benzene solution of the chloride with mercury under a nitrogen atmosphere. The benzene used was the constant boiling portion of thiophene free benzene distilled through columns of ten theoretical plates or better and subsequently dried over sodium.

For the reactions in which the triphenylmethyl solution was used directly, the solutions were analyzed either by the benzoyl peroxide method,<sup>14</sup> or by the oxygen absorption method.<sup>15</sup>

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14. G. S. Hammond, A. Ravve, F. J. Modic, Anal. Chem. 24, 1373, (1952).

15. M. Gomberg, Ber. 33, 3150, Ber 37, 3538-47.

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Because of personal preference, the latter was used exclusively in the study of all the reactions of trityl. The earlier runs were made in a non thermostated absorption apparatus and therefore are not as accurate as some of the later determinations.

Crystalline hexaphenylethane was sought after in various ways. An apparatus similar to Gomberg's<sup>16</sup> was constructed, but

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16. M. Gomberg and Cone Ber. 37, 2033-51.

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for some reason the triphenylmethyl could not be crystallized satisfactorily. Yellow solids containing relatively large amounts of peroxide were the only products obtainable. A dry box flushed with Argon was tried, but with little success. Apparently a complete exclusion of oxygen is extremely difficult. Finally, a high vacuum system was constructed. Recrystallization was tried by distilling solvents from one part of the system to another, and filtration was conducted by creating unequal pressures within the system by means of solvent reservoirs and stopcocks. Even though care was taken to thoroughly evacuate the system initially and to use solvents distilled under inert gases, it was found that the longer and more numerous the operations the more impure the product obtained. The best result obtained was a three day procedure in which the solid residue left after evaporating off the benzene was washed with acetone. This resulted in a white solid which gradually turned yellow while still in the system. Analysis showed that 99.2% of the weight was radical. This does not take into account the absorption of oxygen by the solid during weighing and transferring. This absorption was found to proceed such that about 20% of one solid sample became converted to oxygenated products in a three hour period. Since hexaphenylethane was still this labile in the crystalline form, further experiments along these lines were discontinued. It was hoped at the time these experiments were started that perhaps it might be possible to stockpile large quantities of pure hexaphenylethane.

Triphenyl-Methyl Quench. (a) A benzene solution of triphenylmethyl which had been prepared, but not used for a month or so was quenched with methanol, iodine and pyridine. The methanol and pyridine were added in slight excess. The supernatant liquid was then washed with approximately 20 cc of distilled water followed by three 20 cc portions of thiosulfate solution. The benzene layer was then dried under vacuum and the residue chromatographed. 1.0561 grams of triphenylmethane and .3402 grams of *p*-benzhydryltetraphenylmethane were recovered. A total of 2.8160 grams were recovered over a range of 118 fractions. The fact that products dribbled out over a wide range of eluents suggests that a number of different compounds existed in the mixture.

(b) A freshly prepared benzene solution of triphenylmethyl was quenched. A relatively large amount of triphenylmethyl ethyl ether was recovered. However, a surprising amount of *p*-benzhydryltraphenylmethane was isolated as well as triphenylcarbinol in somewhat lesser amounts. Although 203 fractions were taken, the above three compounds seem to predominate.

(c) A freshly prepared benzene solution of triphenylmethyl was quenched with *N*-acetyethanolamine, but only oily and colored products resulted.

(d) Triphenylmethyl solutions react with oxygen as described by Gomberg.<sup>17</sup> That the reaction gives side products besides the

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17. M. Gomberg, Ber. 37, 3538-47.

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main product of ditritylperoxide has been confirmed. The solution slowly decomposing in the dry box in the presence of a very small amount of oxygen gave more side products than the exposure to atmospheric conditions. Gomberg states that the reaction of trityl with gaseous oxygen is complete in two minutes. However, it was found for a trityl and nitrosobenzene reaction mixture that 12 minutes are required for a maximum oxygen absorption even with vigorous stirring.

Nitrobenzene. (a) Equal molar quantities of nitrobenzene and triphenylmethyl were mixed. After two months, the solution still absorbed oxygen. Before the reaction mixture could be worked up, several more months elapsed and the benzene had diffused out through the rubber stopper and stopple. The solid residue was taken up with acetone which left a solid residue whose melting point corresponded to that of peroxide. The acetone was then evaporated off and the residue steam distilled. A total of 0.165 grams of nitrobenzene was recovered as compared to 0.196 grams of nitrobenzene originally introduced. Of the total products recovered, the identified portions were ditritylperoxide, 0.1562 grams (6.5% of total), nitrobenzene 0.165 grams (6.9%), triphenylmethane 0.6526 grams (27.2%), *p*-benzhydryltetraphenylmethane .2409 grams (10%), and triphenylcarbinol 0.8680 grams (36.4%).

(b) Nitrobenzene was distilled into a flask containing solid hexaphenylethane in vacuum rack. The nitrobenzene was

removed by distillation under vacuum at room temperature. After 10 days, when only solid residue remained, the flask was taken off of rack and a portion of the sticky solid analyzed by oxygen absorption. It was found that 27.2% of weight was still radical. When flask with solid was allowed to stand exposed to the atmosphere, the solid which was originally a light yellow color turned to a dark brown and finally to black. This black tar was dissolved in acetone and transferred to an Erlenmeyer flask. Peroxide was filtered off. At this point peroxide continued to form and was also removed by filtration. Total peroxide recovered .2394 grams. Of the chromatographic fractions the following were identified; triphenylmethane 0.2053 grams, p-benzhydryltetraphenylmethane 0.2088 grams, and triphenylcarbinol .8796 grams. The unidentified fractions total another .3785 grams.

(c) Nitrobenzene and triphenylmethyl were mixed in the vacuum rack under conditions similar to that used in (b). This time the mixture was allowed to stand under vacuum for thirty days. The main quantity of nitrobenzene came off in about six days. After that time a more or less constant small amount collected in the trap every day. This small amount was still collecting at the end of the thirty day period when the vacuum system was accidentally broken. The solid residue was yellow and quite hard. A sample was obtained for analysis by drilling a hole in the solid with a spatula. This was so that a representative sample, not just the solid occurring on the surface,



could be obtained. On oxygenation 32.4% of the weight of the sample was found to be apparent triphenylmethyl. After one day the solid acquired an orange color on its surface. After three days, analysis showed only 18.5% triphenylmethyl activity. The surface had become somewhat sticky, but the interior portions were still a dry yellow solid.

The mixture was then taken up in about 100 cc of acetone and the insoluble material filtered off. This was assumed to be the peroxide, but may have contained some *p*-benzhydriyltetraphenylmethane. This acetone insoluble part weighed 2.5367 grams. In filtration, some of the filtrate was accidentally spilled so that the remainder of the products could only be determined in a relative manner. After stripping off the acetone from the filtrate, the residue was vacuum distilled using a temperature of 80 to 85°. Nitrobenzene was obtained. The weight after removal of a sample for refractive index determination was 0.632 g. Chromatography of the residue on alumina yielded triphenylmethane, 0.3696 grams (19% of products recovered), and *p*-benzhydriyltetraphenylmethane, 0.2357 grams (12%). Fractions corresponding to approximately 30% of the products recovered appear to be triphenylcarbinol although characterization has not been completed. A total of 18 per cent of the acetone soluble solid was obtained in identifiable fractions.

Nitrosobenzene. Nitrosobenzene was prepared using directions found in Organic Synthesis.<sup>18</sup> Purification was carried out by

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18. Organic Synthesis, Vol. 25, 80.

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recrystallizing from alcohol or by subliming. Better looking material was obtained by sublimation.

A reaction was carried out using equimolar quantities of nitrosobenzene and triphenylmethyl. Trityl activity declined fairly rapidly at first, but then leveled off. The reaction mixture still absorbed some oxygen after two weeks. Products identified from the various oxygenated fractions were azoxybenzene, p-benzhydryltetraphenylmethane, triphenylcarbinol, triphenylmethane, and possibly tetraphenylmethane. The main reaction was set aside and lost in the period of interest in other fields.

The appearance of azoxybenzene from this reaction mixture is not surprising since a study of the thermal decomposition products of nitrosobenzene shows that a large portion of the products formed is azoxybenzene. A sample of nitrosobenzene which had stood in an open bottle in the lab for some time had turned to a dark black tarry oil. This was poured on several inches of alumina and successively eluted with solvents of greater polarity ranging from Skellysolve B to benzene. Of the total solids obtained, 70 percent was found to be azoxybenzene.

Trinitrobenzene. An excess of Eastman white label trinitro benzene was mixed with triphenylmethyl in benzene. The trityl activity decreased very rapidly at first, but it is difficult to say whether this was due to a reaction or to an inadvertant inclusion of air into the reaction flask. After the initial decrease the activity remained fairly constant. The reaction is currently being worked up for products so the results

are far from conclusive. However, it appears that triphenylmethane is obtained in smaller quantities than in the nitrobenzene reactions and that *p*-benzhydryltetraphenylmethane is missing. Triphenylcarbinol is obtained, but the relative quantity is undetermined.

Reaction of Ditriphenylmethyl Peroxide With Sulfuric Acids.

The ditriitylperoxide was obtained by air oxidizing benzene solutions of triphenylmethyl. This crude product was recrystallized by dissolving in boiling dioxane to the extent of .7 gm. per 100 cc of solvent and immediately ceasing further heating. The solution on standing overnight gave the crystals desired.

After the recrystallized peroxide was dried in a vacuum dessicator, 1.5798 gms. were weighed out. About 25 cc of concentrated  $H_2SO_4$  was then added. A dark black mixture was obtained which did not noticeably turn warm. After 10 minutes, crystals were still floating around in the sulfuric acid. After about a half an hour, a homogeneous solution appeared to have resulted so the mixture was poured on 500 cc of chopped ice. The light brown solid was filtered on a Buchner and sucked free of excess water. The solid was then dissolved in ether, the ether dissolving all but a small amount of colored residue on the filter paper. The ether solution was washed with two portions of dilute KOH, the first portion giving a brown colored aqueous phase and the second portion a relatively clear aqueous layer indicating that the separation was essentially complete.

On acidification of the base solution, the color changed to a light straw color. This acidified solution was extracted with ether. On the third extraction, the ether was colorless although the aqueous solution was still slightly colored. This aqueous solution would not decolorize bromine water. The ether fractions were dried with calcium chloride and evaporated down to about 50 cc. The neutral fraction was further evaporated to about 20 cc and Skelly A added. No precipitate formed as Gomberg<sup>19</sup>

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19. Gomberg, Ibid.

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reported. However on standing for two days, beautiful rhomboidal crystals formed. These were filtered and weighed. Weight .7070 gms. On drying in vacuum dessicator overnight, there was no weight loss. A second and third crop of crystals were obtained weighing .2777 and .4040 gms. respectively. The residue after evaporating off the mother liquor weighed .1133 gms. The residue of the base soluble fraction weighed .0908 gms. These fractions represent a total 1.5528 gms. of recovered products from the 1.5798 gms. of peroxide originally reacted.

Benzophenone was searched for in the mother liquor residue by washing with  $\text{CCl}_4$  and taking infra red spectra of the  $\text{CCl}_4$  solution. The excess  $\phi_3\text{COH}$  was not very soluble in  $\text{CCl}_4$ . Attempts were made to make carbonyl derivatives (oxime, semicarbazone) from synthetic mixtures but were not uniformly successful. Attempts to separate a synthetic mixture by chromatography also failed, at least in its quantitative aspects.

The base soluble portion was found to absorb bromine with evolution of HBr. However, efforts to sublime phenol failed even though in synthetic mixtures containing phenol, the phenol could readily be separated by sublimation techniques. This residue was then dissolved in acetone and evaporated on a salt plate in order to obtain infra-red spectrum.

### RESULTS

The yield of triphenylcarbinol in this experiment was 86.7% of actual weighed material. Estimates run the yield up as high as 91% basing the calculations on 2 moles of  $\phi_3\text{COH}$  as being theoretically obtainable from each mole of peroxide.

Benzophenone was found in the mother liquor. Although neither the compound nor its derivative could be isolated, an estimate of .0136 gms. was made by applying Beer's law to the carbonyl frequency of the infra-red spectrum. The estimate of 91% for the triphenylcarbinol is obtained by assuming that what is not benzophenone is the neutral fraction is triphenylcarbinol.

Phenol could not be isolated although its absence should not be inferred from this failure. The residue was dried by placing in a vacuum dessicator and pumping on it overnight. The phenol if present, could well have sublimed off during this procedure. The interesting observation is that there is some phenolic substance present which is not the simple phenol. This was shown by the non-sublimable solid absorbing bromine

with evolution of HBr. The I. R. shows that there might also be some sulfonated product present in this acidic fraction. The  $\text{O}_3\text{C}$ -grouping, if present at all, is certainly not a major constituent. All of the triphenylmethyl type compounds, but one, in our collection show strong bands at  $13.2\mu$  and  $14.3\text{-}14.4\mu$ . There is a questionable bump in the spectrum in question at  $13.2$  and one at  $14.2$ .

Methacrylonitrile was washed with two percent aqueous sodium hydroxide and with water to remove the stabilizer. After drying over calcium chloride the monomer was distilled through an efficient column under nitrogen. Material boiling at  $88.5\text{-}90^\circ$ ,  $n_D^{25}$ , 1.3980 was used for subsequent studies.

Polymerization Experiments. Solutions were prepared by dissolving weighed amounts of azo-bis-isobutyronitrile in methacrylonitrile. Samples were placed in constricted test tubes which had been carefully cleaned and dried. Each sample was degassed by freezing in a dry ice-acetone bath, evacuating and flushing with nitrogen, the entire procedure being repeated three times and the tubes were finally evacuated and sealed. The samples were heated in a thermostat at  $62.5^\circ$ . At intervals tubes were removed, cooled and opened. Polymer was precipitated by pouring the sample into methanol. The polymer was then reprecipitated twice by dissolving it in acetone and pouring it into methanol. Samples were then dried to constant weight.

Viscosity measurements were made with acetone solutions in an Ostwald viscometer having a flow time of 110 sec. at 25°. Intrinsic viscosities  $[\eta]$  were calculated from the relationship,  $N_{sp}/C = N$ , where C is the concentration of polymer in grams per 100 ml. The results reported in Table \_\_\_ were obtained by extrapolation to infinite dilution.

TABLE V

Polymerization of Methacrylonitrile in bulk at 62-5°

Run	$[\text{AIB}]_0 \times 10^3$ moles/liter	$[\text{AIB}]^{\frac{1}{2}} \times 10^2$	Polymerization Rate, in percent per hr.	N
5	87.6	29.6	1.944	0.13
6	29.2	17.1	1.230	0.20
7	14.6	12.1	1.017	0.85
8	9.73	9.86	0.800	0.85
9	7.96	8.92	0.723	0.99
10	5.97	7.73	0.646	---

Our work confirms previous reports (20) showing that the

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20. W. Kern and H. Fernow, J. Prakt. Chem. 160, 302 (1942).

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temperature interval 60-65° is convenient for the study of methacrylonitrile polymerization. The product obtained is white and granular and the polymerization rates at low conversions are proportional to the square root of the initiator concentration as is readily derived from the data in Table V.

### Discussion

These results will be treated in detail in forthcoming publications but the significant conclusions or indications will be pointed out at this time.

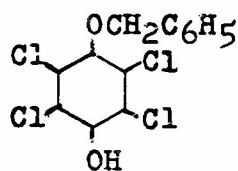
A major emphasis has been placed upon the study of "cage effects" in thermal decomposition reactions. Such effects have been frequently suggested as being of importance in determining the fate of radical pairs produced in thermal decompositions and the concept has met with rather varying response. It has been our experience that much better understanding is achieved by referring to the phenomena by the more cumbersome but also more specific designation of diffusion control of the fate of primary decomposition products. The concept of diffusion control of reactions such as the recombination of reactive free radicals is commonly accepted and the "cage effect" can be no more nor less than the microscopic reverse of the former phenomenon. Using this as a guide we are able to draw up some rough criteria as to the probability of occurrence of important cage effects in decomposition reactions. The reaction which is believed to be subject to diffusion control must necessarily be one whose rate is likely to be as fast or faster than diffusion rates in liquids. This criterion may furthermore be modified somewhat to take account of dipole-dipole attraction which may operate in such a way as to prolong contact between primary products which have large dipoles (such as cyanoalkyl and acyloxy



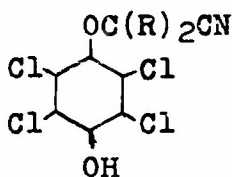
radicals), especially when they are produced in media with low dielectric constants.

In a reinvestigation of the decomposition of di-tert-alkyl peroxides we have failed to confirm the conclusions of Kherasch and coworkers ( 5 ) that the fate of a given alkoxy radical is influenced strongly by the identity of the parent peroxide. Variations in the ketone/alcohol ratio (Table I) may occur but are small enough to tax our analytical method. The chosen method of analysis is designed to be much more accurate than that employed by the earlier workers and was carefully tested for accuracy and precision. Since we have neither confirmed the results in the literature nor established that no variations occur it will be necessary to defer final judgement (and publication) until further investigations can be completed. At the present time we feel that there is no unequivocal evidence for proximity effects in the decomposition of dialkyl peroxides in cumene.

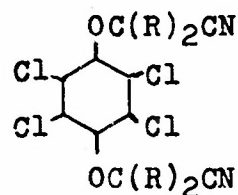
The study of the scavenging of primary products of the decomposition of bis-azonitriles by chloranil turned up a very interesting phenomenon which was apparently missed completely by Eickel and Waters ( 2 ). This is the fact that in toluene solution the following compounds are produced from chloranil.



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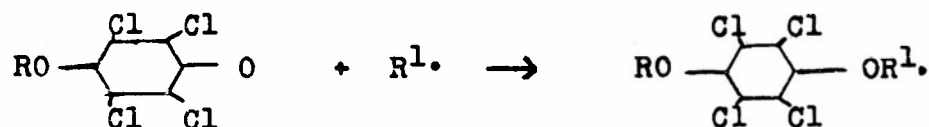


II



III

Compound III is the only diether found after an exhaustive search and we are convinced that the unsymmetrical diether and the dibenzyl ether were not produced in significant amounts. This observation is difficult to reconcile with the rather obvious mechanism for diether formation shown by equation (1). This



would require that the semiquinone radical with a benzyl group attached to oxygen have a very different relative reactivity in hydrogen abstraction and radical coupling reactions than the semiquinone in which R is the cyanoalkyl group. Two explanations have been considered. The first is that two cyanoalkyl radicals produced in the thermal decomposition become attached to chloranil before they have been separated by diffusion. The second, which is suggested by other work in these laboratories, is that the diether is formed, not by the attack of a radical on a semiquinone but by the reaction of a radical with a molecular complex of chloranil with a radical. We hope that more study can be devoted to the problem but intend to publish the completed results shortly.

The very careful reinvestigation of the system nitrobenzene-triphenylmethyl has shown that the previously reported oxidation of triphenylmethyl by nitrobenzene can not be repeated. We can only conclude that Dr. Raave's early work was misleading either because of the spurious inclusion of unknown catalytic

materials or because of his inaccurate observation of experimental results.

The study of methacrylonitrile polymerization was initiated with the intention of comparing the chain transfer activity of growing radical chains with that of analogous tertiary cyanoalkyl radicals produced in the decomposition of azonitriles. Since the data for the latter is available (see accompanying manuscript) for butyl mercaptan as a transfer agent, it is anticipated that Dr. Sen will be able to complete the study within the next few months as he will continue the work for a short time with support from another source.

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